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(54) Title: A COMPOSITION CONTAINING A CROSS-LINKABLE MATRIX PRECURSOR AND A PORAGEN, AND A POROUS MATRIX PREPARED THEREFROM (57) Abstract <p>A suitable cross-linkable matrix precursor and a poragen can be treated to form a porous cross-linked matrix having a T_g of greater than 300 °C. The porous matrix material has a lower dielectric constant than the corresponding non-porous matrix material, making the porous matrix material particularly attractive for a variety of electronic applications including integrated circuits, multichip modules, and flat panel display devices.</p>		

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A COMPOSITION CONTAINING A CROSS-LINKABLE MATRIX PRECURSOR AND A
PORAGEN, AND A POROUS MATRIX PREPARED THEREFROM

This application claims the benefit of United States Provisional Application
5 Serial No. 60/109,710 filed on November 24, 1998.

The present invention relates to a composition that contains a cross-linkable
matrix precursor and a poragen, and a porous matrix prepared therefrom.

As semiconductor devices become smaller and smaller, and chip packing
densities increase correspondingly, undesirable capacitance related delays and cross-talk
10 between metal interconnects are more acutely manifested. Since capacitance related
delays and cross-talk relate to the dielectric constant of the insulator, attention has focused
on the creation of ultra-low dielectric constant materials (that is, dielectric materials having
dielectric constants of ≤ 2.0). Such efforts include creating porous inorganic (for example,
silicon dioxide) or thermoplastic polymeric (for example, polyimide) materials.

15 Silicon dioxide, which has been the dominant inter-level dielectric material
(ILD) for the past 40 years, can be made porous by well-developed sol-gel techniques such
as those disclosed in *Proc. Mat. Res. Soc.* **381**, 261 (1995); *Proc. Mat. Res. Soc.* **443**, 91
(1997); and *Proc. Mat. Res. Soc.* **443**, 99 (1997). Although the introduction of pores into
silicon dioxide causes a reduction of dielectric constant from 4.2 to less than 2.0, the
20 resultant porous material is significantly weakened. Thus, porous silicon dioxide is
impractical as a low dielectric constant material.

Porous thermoplastic polymers, particularly thermally stable polymers such as
polyimides, have also been investigated for use as ultra-low dielectric materials. See, for
example, U.S. Patents 5,895,263 and 5,776,990. Although these porous thermoplastic
25 materials can be made to have acceptable dielectric constants, the pores tend to collapse
during subsequent high temperature processing, thereby precluding the use of these
materials for the applications of interest.

In view of the deficiencies in the art, it would be desirable to have an ultra-low
dielectric material that is stable to the severe processing conditions required in fabricating
30 semiconductors.

The present invention addresses the problems of the prior art by providing a
composition comprising a) a hydrocarbon-containing matrix precursor; and b) a poragen;
wherein the matrix precursor is selected to form upon curing a cross-linked, hydrocarbon-
containing material having a T_g of greater than 300°C. The cross-linked hydrocarbon-
35 containing material preferably has a thermal stability of at least 400°C.

In a second embodiment, the present invention is a low dielectric constant material comprising a porous cross-linked hydrocarbon-containing matrix having a T_g of greater than 300°C. The material is preferably in the form of a thin film on a substrate.

In a third embodiment, the present invention is a method of making a porous
5 film on a substrate comprising:

coating on a substrate, a solution comprising a matrix precursor which cures
to form a matrix material having a T_g of at least 300°C, a poragen, and a solvent;

removing the solvent;

reacting the matrix precursor to form the matrix material; and

10 degrading the poragen to form pores in the matrix. The removing, reacting,
and degrading steps are performed by one or more heating steps as will be more
thoroughly described below.

In a fourth embodiment, the present invention is an integrated circuit article
comprising an active substrate containing transistors and an electrical interconnect structure
15 containing patterned metal lines separated, at least partially, by layers or regions of a
porous dielectric material, wherein the dielectric material comprises a cross-linked
hydrocarbon-containing matrix having a T_g of greater than 300°C.

The present invention solves a problem in the art by providing a low dielectric
constant, porous matrix material that is suitable as an interlayer dielectric for
20 microelectronics applications and stable to processing temperature of greater than 300°C.

B-Staged - refers to a partially polymerized monomer, or a mixture of
monomer and partially polymerized monomer. A b-staged product is usually synonymous
with "prepolymer" or "oligomer."

Cross-linkable - refers to a matrix precursor that is capable of being
25 irreversibly cured, to a material that cannot be reshaped or reformed. Cross-linking may be
assisted by UV, microwave, x-ray, or e-beam irradiation. Often used interchangeably with
"thermosettable" when the cross-linking is done thermally.

Matrix precursor - a monomer, prepolymer, or polymer, or mixtures thereof
which upon curing forms a cross-linked Matrix material.

30 Monomer - a polymerizable compound or mixture of polymerizable
compounds.

Functionality - refers to the number of groups in a monomer available for
polymerization. For example, a biscyclopentadienone and a bis-acetylene each have a
functionality of 2, while the monomer 1,1,1-tris(4-trifluorovinylphenoxy)ethane has a
35 functionality of 3.

Hydrocarbon-containing - refers to a matrix or matrix precursor that contains carbon and hydrogen, but may contain other elements. The matrix or matrix precursor preferably contains not more than 50 weight percent silicon, more preferably not more than 30 weight percent silicon, and most preferably not more than 20 weight percent silicon.

5 Poragen - a solid, liquid, or gaseous material that is removable from a partially or fully cross-linked matrix to create pores or voids in a subsequently fully cured matrix, thereby lowering the effective dielectric constant of the resin.

Thermal stability temperature - the maximum temperature, T, at which the weight loss of a sample maintained at that temperature in an inert environment is less than 1
10 percent per hour .

Matrix - a continuous phase surrounding dispersed regions of a distinct composition. In the final article, the matrix is a solid phase surrounding dispersed voids or pores.

The porous matrix of the present invention can be prepared from a mixture of
15 a poragen and a cross-linkable hydrocarbon-containing matrix precursor. The poragen may be reactive, so that the poragen becomes chemically bonded into the polymer matrix, or it may be non-reactive.

Suitable matrix precursors are those that form cross-linked resins having a T_g of greater than 300°C and more preferably greater than 350°C.

20 Preferably, the matrix precursors are further characterized in that they experience either no decrease or only relatively small decreases in modulus during cure. If the material experiences large modulus drops during cure, especially if the low modulus occurs at temperatures near the degradation temperature of the poragen, pore collapse may occur.

25 One preferred class of matrix precursors include thermosettable benzocyclobutenes (BCBs) or b-staged products thereof, such as those described in U.S. Patent 4,540,763 and U.S. Patent 4,812,588. A particularly preferred BCB is 1,3-bis(2-bicyclo[4.2.0]octa-1,3,5-trien-3-ylethynyl)-1,1,3,3-tetramethyldisiloxane (referred to as DVS-bisBCB), the b-staged resin of which is commercially available as CYCLOTENE™ resin
30 (from The Dow Chemical Company).

Another second preferred class of matrix materials include polyarylenes. Polyarylene, as used herein, includes compounds that have backbones made from repeating arylene units and compounds that have arylene units together with other linking units in the backbone, for example oxygen in a polyarylene ether. Examples of
35 commercially available polyarylene compositions include SiLK™ Semiconductor Dielectric

(from The Dow Chemical Company), Flare™ dielectric (from Allied Signal, Inc.), and Velox™ (Poly(arylene ether)) (from AirProducts/Shumacher). A preferred class of polyarylene matrix precursor is a thermosettable mixture or b-staged product of a polycyclopentadienone and a polyacetylene, such as those described in WO 98/11149. Examples of the thermosetting compositions or cross-linkable polyarylenes that may be used in the composition of this invention include monomers such as aromatic compounds substituted with ethynyl groups ortho to one another on the aromatic ring as shown in WO 97/10193; cyclopentadienone functional compounds combined with aromatic acetylene compounds as shown in WO 98/11149; and the polyarylene ethers of U.S. Patent Nos. 5,115,082; 5,155,175; 5,179,188 and 5,874,516 and in PCT WO 91/09081; WO 97/01593 and EP 0755957-81. More preferably, the thermosetting compositions comprise the partially polymerized reaction products (that is, b-staged oligomers) of the monomers mentioned above (see for example, WO 98/11149, WO 97/10193).

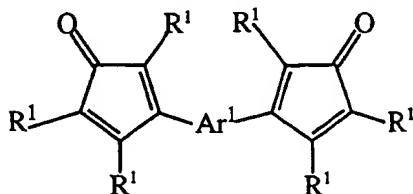
Preferably, the polyarylene precursors are characterized by a modulus profile as measured by torsional impregnated cloth analysis (TICA) characterized in that during heating of the composition a Minimum Measured Modulus observed in the temperature range from 300 to 400°C occurs at a temperature T_{min} , and said Minimum Measured Modulus is greater than a value equal to 20 percent, more preferably 50 percent, of a Measured Cured Modulus of the composition after heating to a maximum temperature and cooling back down to T_{min} . "Measured Heat-up Modulus" is the modulus at a given temperature detected for the test composite during the heating phase of the test on a plot of modulus versus temperature. "Minimum Measured Heat-up Modulus" is the minimum Measured Heat-up Modulus occurring in the temperature range of 300 to 450°C. "Measured Cured Modulus" is the modulus at a given temperature for the test composite during the cool down phase. In this TICA technique, a woven glass cloth (preferably, 0.3 mm thick, 15 mm wide, and 35 mm long for example, TA Instruments part number 980228.902) is mounted in a dynamic mechanical analyzer, such as a DuPont 983 DMA, preferably fitted with a Low Mass Vertical Clamp Accessory or equivalent functionality to enhance sensitivity. The ends of the cloth are wrapped in aluminum foil leaving 10 mm in length exposed. The cloth is then mounted in the vertical clamps of the dynamic mechanical analyzer which are set 10 mm apart. The clamps are tightened to 12 inch (34.48 cm) pounds using a torque wrench. The cloth is impregnated using a solution comprising the precursor compounds at 10 to 30 percent solids via a pipet. The cloth is thoroughly soaked with the solution and any excess is removed using the pipet. A heat deflector and oven are attached and a nitrogen flow of 3 standard cubic feet per hour is

established. Amplitude of the displacement is set to 1.00 mm and frequency to 1 Hz. The sample is heated to 500°C at 5°C per minute and then allowed to cool. Data is collected during both the heating and cooling stages. Data analysis may be performed to obtain temperature versus flexural modulus values for the composite of glass and formulation.

- 5 Prepared software programs such as DMA Standard Data Analysis Version 4.2 from DuPont or Universal Analysis for Windows 95/98/NT Version 2.5H from TA Instruments, may be used to perform the data analysis. The modulus values themselves are not absolute values for the tested formulation due to the contribution of the glass cloth and the unavoidable variation in sample loading. However, using ratios of the modulus value at a point during heating to a modulus of the composite after cure and cool down to some consistent temperature gives a value, which can be used to compare different formulations. See also copending, co-owned U.S. Application Serial No. _____, having attorney docket number 44528.

- 15 Preferred polyarylene-type matrix precursors comprise the following compounds, or more preferably, a partially polymerized (b-staged) reaction product of the following compounds:

(a) a biscyclopentadienone of the formula:

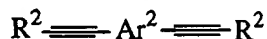


(b) a polyfunctional acetylene of the formula:

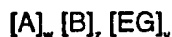


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(c) and, optionally, a diacetylene of the formula:

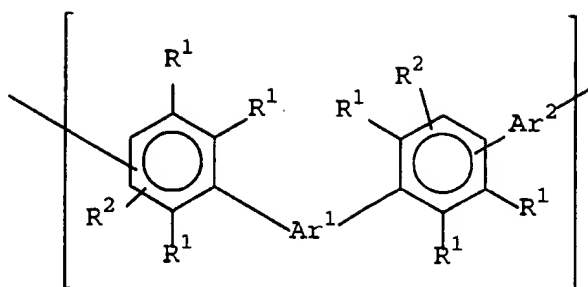


- 25 wherein R¹ and R² are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar¹, Ar² and Ar³ are independently an unsubstituted aromatic moiety, or inertly-substituted aromatic moiety, and y is an integer of three or more. Stated alternatively, the most preferred matrix precursor material comprises a curable polymer of the formula:

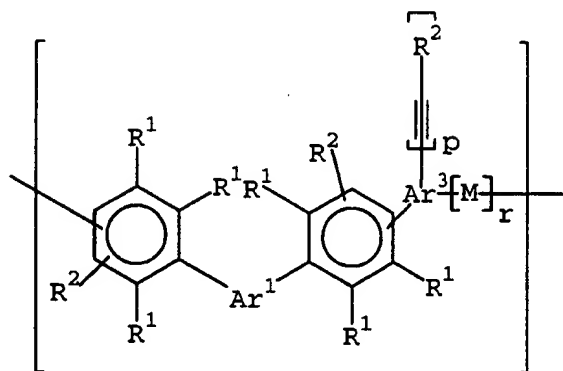


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wherein A has the structure:

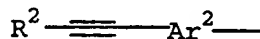
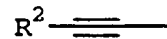
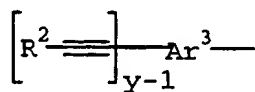
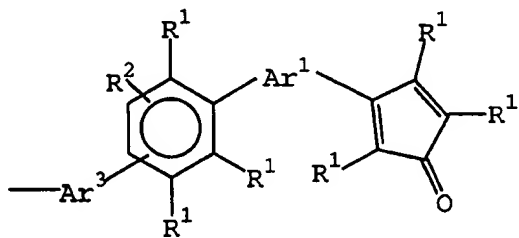
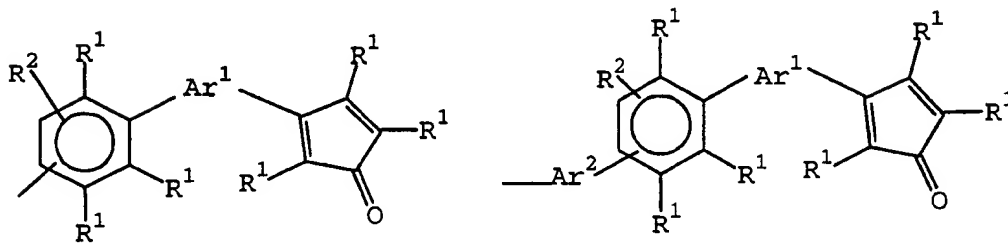


and B has the structure:



end groups EG are independently represented by any one of the formulas:

EG=



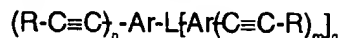
wherein R^1 and R^2 are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar^1 , Ar^2 and Ar^3 are independently an unsubstituted aromatic moiety or inertly-substituted aromatic moiety and M is a bond, y is an integer of three or more, p is the number of unreacted acetylene groups in the given mer unit, r is one
5 less than the number of reacted acetylene groups in the given mer unit and $p+r=y-1$, z is an integer from 1 to 1000; w is an integer from 0 to 1000 and v is an integer of two or more.

When the matrix precursor comprises a thermosettable mixture or b-staged product of a polycyclopentadienone and a polyacetylene, the precursors preferably are characterized so that branching occurs relatively early during the curing process. Formation
10 of a branched matrix early on in the cure process minimizes the modulus drop of the matrix, and helps minimize possible pore collapse, during the cure process, and/or allows for use of poragens that decompose or degrade at lower temperatures. One approach for achieving this is to use a ratio of cyclopentadienone functionality to acetylene functionality in the precursor composition of greater than 3:4, and preferably less than 2:1, more preferably 1:1.

15 A matrix precursor comprised of 3 parts 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) and 2 parts 1,3,5-tris(phenylethynyl)benzene (molar ratios) is an example of such a system. Alternatively, additional reagents capable of cross-linking the thermosettable mixture or b-staged product of a polycyclopentadienone and a polyacetylene can be added to minimize the modulus drop of the matrix during the cure
20 process. Examples of suitable reagents include bisorthodiacetylenes as disclosed, for example, in WO 97/10193; monoorthodiacetylenes; bistriazenes; tetrazines, such as 1,3-diphenyltetrazine; bisazides, such as bisulfonylazides; and peroxides, including diperoxides. The loading levels of the reagent can vary from <1 weight percent based on solids to >30 weight percent based on solids.

25 A third example of a matrix precursor suitable for the preparation of the porous matrix of the present invention is a thermosettable perfluoroethylene monomer (having a functionality of 3 or more) or a b-staged product thereof, the disclosure and preparation of which can be found in U.S. Patent 5,023,380 (col. 4, starting on line 38), and U.S. Patent 5,540,997 (col. 3, lines 4 to 46). A preferred thermosettable perfluoroethylene
30 is 1,1,1-tris(4-trifluorovinylphenoxy)ethane. The thermosettable perfluoroethylene monomer may also be conveniently copolymerized with a perfluoroethylene monomer having a functionality of two, prepared as described in U.S. Patents 5,021,602; 5,037,917; and 5,246,782.

Another polyarylene matrix precursor is a thermosettable bis-*o*-diacetylene or b-staged product thereof as described in WO 97/10193. According to this embodiment the precursor comprises a compound of the formula



- 5 wherein each Ar is an aromatic group or inertly-substituted aromatic group and each Ar comprises at least one aromatic ring; each R is independently hydrogen, an alkyl, aryl or inertly-substituted alkyl or aryl group; L is a covalent bond or a group which links one Ar to at least one other Ar; preferably a substituted or unsubstituted alkyl group, n and m are integers of at least 2; and q is an integer of at least 1, and wherein at least two of the
10 ethynyl groups on one of the aromatic rings are *ortho* to one another.

Poragens and Methods of Forming Porous
Cross-linked Dielectrics

- The poragen materials are materials that will form domains (or discrete regions) in the matrix or matrix precursor. Preferably, the domains should be no larger than
15 the final desired pore size.

Many polymeric materials may be useful as poragens. However, a poragen that functions well with a first matrix system will not necessarily function well with another matrix system. The compatibility poragen with the matrix system must be high enough that very large domains are not formed but cannot be so high that no domains are formed.

- 20 The poragens useful in this invention are preferably those that thermally degrade (that is, burnout) at temperatures below the thermal stability temperature of the matrix material. The degradation temperature range may overlap with the curing temperature range so long as curing occurs more quickly than (or before) degradation allowing the matrix to set before the poragen is substantially removed. These materials
25 preferably decompose primarily into low molecular weight species and, thus, do not leave substantial "char" in the porous matrix.

Examples of poragens and methods by which they can be used in conjunction with the matrix precursor to form porous cross-linked matrix materials are described as follows.

- 30 The poragen may be a block copolymer (for example, a di-block polymer). Such materials may be capable of self-assembling, as described in *Physics Today*, February 1999, p. 32, if the blocks are immiscible to give separated domains in the nanometer size range. Such a block copolymer can be added to the cross-linkable matrix precursor with or without solvent to obtain a formulation suitable for processing. The block
35 copolymer can self-assemble during processing (for example, after spin coating, but before

the matrix is formed). One or more of the blocks may be reactive with the matrix or the blocks may be non-reactive. One or more of the blocks may be compatible with the matrix, or its precursor, but preferably at least one block is incompatible with the matrix. Useful polymer blocks can include an oligomer of the matrix precursor, polyvinyl aromatics, such as polystyrenes, polyvinylpyridines, hydrogenated polyvinyl aromatics, polyacrylonitriles, polyalkylene oxides, such as polyethylene oxides and polypropylene oxides, polyethylenes, polylactic acids, polysiloxanes, polycaprolactones, polycaprolactams, polyurethanes, polymethacrylates, such as polymethylmethacrylate or polymethacrylic acid, polyacrylates, such as polymethylacrylate and polyacrylic acid, polydienes such as polybutadienes and polyisoprenes, polyvinyl chlorides, polyacetals, and amine-capped alkylene oxides (commercially available as Jeffamine™ polyether amines from Huntsman Corp.) For example, a diblock polymer based on polystyrene and polymethylmethacrylate can be added to a solution of CYCLOTENE resin in a suitable solvent such as mesitylene at a weight:weight ratio of resin to diblock polymer of preferably not less than 1:1, and more preferably not less than 2:1, and most preferably not less than 3:1. The overall solids content is application dependent, but is preferably not less than 1, more preferably not less than 5, and most preferably not less than 10 weight percent, and preferably not greater than 70, more preferably not greater than 50, and most preferably not greater than 30 weight percent. The solution can then be spin-coated onto a silicon wafer leaving a thin film containing a dispersed phase of diblock copolymer in a continuous phase of DVS-bisBCB. The film can then be thermally cured leaving a crosslinked polymer system containing a dispersed phase of poly(styrene-b-methylmethacrylate) in a continuous phase of cross-linked DVS-bisBCB. The diblock copolymer can then be decomposed or removed to leave a porous cross-linked DVS-bisBCB polymer. Similarly, a diblock polymer based on polystyrene and polybutadiene can be added to a b-staged solution of a dicyclopentadienone (for example, 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone)) and a trisacetylene (for example, 1,3,5-tris(phenylethynyl)benzene).

Thermoplastic homopolymers and random (as opposed to block) copolymers may also be utilized as poragens. As used herein, "homopolymer" means compounds comprising repeating units from a single monomer. Suitable thermoplastic materials include polystyrenes, polyacrylates, polymethacrylates, polybutadienes, polyisoprenes, polyphenylene oxides, polypropylene oxides, polyethylene oxides, poly(dimethylsiloxanes), polytetrahydrofurans, polyethylenes, polycyclohexylethylenes, polyethyloxazolines, polyvinylpyridines, polycaprolactones, polylactic acids, copolymers of these materials and

mixtures of these materials. The thermoplastic materials may be linear, branched, hyperbranched, dendritic, or star like in nature.

Polystyrene has been found to be particularly suitable with thermosettable mixtures or b-staged products of a polycyclopentadienone and a polyacetylene, such as those described in WO 98/11149, because it decomposes at a high temperature (for example, around 420°C to 450°C) and also decomposes primarily into the monomer which can then diffuse out of the matrix. Any known polystyrene may be useful as the porogen. For example, anionic polymerized polystyrene, syndiotactic polystyrene, unsubstituted and substituted polystyrenes (for example, poly(α -methyl styrene)) may all be used as the porogen. Unsubstituted polystyrene is especially preferred.

For example, an anionically polymerized polystyrene with a number average molecular weight of 8,500 can be blended with a polyarylene b-staged reaction product of a polycyclopentadienone and a polyacetylene. This solution can then be spin-coated onto a silicon wafer to create a thin film containing the dispersed phase of polystyrene in the polyarylene matrix precursor. The coated wafer is cured on a hot plate to form the matrix, then the polystyrene porogen is removed by thermal treatment in an oven to form a porous polyarylene matrix.

The porogen may also be designed to react with the cross-linkable matrix precursor during or subsequent to b-staging to form blocks or pendant substitution of the polymer chain. Thus, thermoplastic polymers containing, for example, reactive groups such as vinyl, acrylate, methacrylate, allyl, vinyl ether, maleimido, styryl, acetylene, nitrile, furan, cyclopentadienone, perfluoroethylene, BCB, pyrone, propiolate, or ortho-diacetylene groups can form chemical bonds with the cross-linkable matrix precursor, and then the thermoplastic can be removed to leave pores. The thermoplastic polymer can be homopolymers or copolymers of polystyrenes, polyacrylates, polymethacrylates, polybutadienes, polyisoprenes, polyphenylene oxides, polypropylene oxides, polyethylene oxides, poly(dimethylsiloxanes), polytetrahydrofurans, polyethylenes, polycyclohexylethylenes, polyethyloxazolines, polycaprolactones, polylactic acids, and polyvinylpyridines or mixtures thereof. A single reactive group or multiple reactive groups may be present on the thermoplastic. The number and type of reactive group will determine whether the thermoplastic porogen is incorporated into the matrix as a pendant material or as a block. The thermoplastic materials may be linear, branched, hyperbranched, dendritic, or star like in nature.

For example, a low molecular weight ($<10,000 M_n$) polypropylene glycol oligomer can be end-capped with cinnamate groups, then added at 10 to 30 weight percent

to a neat DVS-bisBCB monomer. This mixture can then be b-staged by heating, then diluted with a suitable solvent such as mesitylene and spin-coated onto a silicon wafer to create a thin film containing a dispersed phase of polypropylene glycol oligomers chemically bonded to the b-staged DVS-bisBCB. The dispersed polypropylene glycol oligomers can then be decomposed to leave a porous cross-linked DVS-bisBCB polymer.

The desired molecular weight of polymeric poragens will vary with a variety of factors, such as their compatibility with the matrix precursor and cured matrix, the desired pore size, etc. Generally, however, the number average molecular weight of the poragen is greater than 2000 and less than 100,000. More preferably the molecular weight is in the range of 5000 to 50,000 and most preferably less than 35,000. The poragen polymer also preferably has a narrow molecular weight distribution.

The poragen may also be a material that has an average diameter of 1 to 50 nm. Examples of such materials include dendrimers (polyamidoamine (PAMAM), dendrimers are available through Dendritech, Inc., and described by Tomalia, et al., *Polymer J.* (Tokyo), Vol. 17, 117 (1985); polypropylenimine polyamine (DAB-Am) dendrimers available from DSM Corporation; Frechet type polyethereal dendrimers (described by Frechet, et al., *J. Am. Chem. Soc.*, Vol. 112, 7638 (1990), Vol. 113, 4252(1991)); Percec type liquid crystal monodendrons, dendronized polymers and their self-assembled macromolecules (described by Percec, et al., *Nature*, Vol. 391, 161(1998), *J. Am. Chem. Soc.*, Vol. 119, 1539(1997)); hyperbranched polymer systems such as Boltron H series dendritic polyesters (commercially available from Perstorp AB) and latex particles, especially cross-linked polystyrene containing latexes. These materials may be non-reactive with the cross-linkable matrix precursor, or reactive as described above. For example, a generation 2 PAMAM (polyamidoamine) dendrimer from Dendritech, Inc. can be functionalized with vinyl benzyl chloride to convert amine groups on the surface of the dendrimer to vinyl benzyl groups. This functionalized dendrimer can then be added to a solution of b-staged DVS-bisBCB in mesitylene, and the mixture can then be spin-coated on a silicon wafer to obtain a dispersed phase of PAMAM dendrimer in DVS-bisBCB oligomers. The film can be thermally cured to obtain a cross-linked polymer system containing a dispersed phase of PAMAM dendrimer chemically bonded to a continuous phase of cross-linked DVS-bisBCB. The dendrimer can then be thermally decomposed to obtain the porous cross-linked DVS-bisBCB polymer. Alternatively, a generation 4 Boltron dendritic polymer (H40) from Perstorp AB can be modified at its periphery with benzoyl chloride to convert hydroxy groups on the surface of the dendrimer to phenyl ester groups. This functionalized dendrimer can then be added to a precursor solution of partially polymerized

(that is, b-staged) reaction product of a polycyclopentadiene compound and a polyacetylene compound in a solvent mixture of gamma-butyrolactone and cyclohexanone. The mixture can then be spin-coated on a silicon wafer to obtain a dispersed phase of Boltron H40 benzoate dendritic polymers in precursor oligomers. The film can be thermally cured to
5 obtain a cross-linked polymer system containing a dispersed phase of dendrimer chemically bonded to a continuous phase of cross-linked polyarylene. The dendrimer can then be thermally decomposed at 400°C to obtain the porous cross-linked polyarylene.

Alternatively, the poragen may also be a solvent. For example, a b-staged prepolymer or partially cross-linked polymer can first be swollen in the presence of a
10 suitable solvent or a gas. The swollen material can then be further cross-linked to increase structural integrity, whereupon the solvent or gas can be removed by applying vacuum or heat. Suitable solvents would include mesitylene, pyridine, triethylamine, N-methylpyrrolidinone (NMP), methyl benzoate, ethyl benzoate, butyl benzoate, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, cyclohexylpyrrolidinone,
15 and ethers or hydroxy ethers such as dibenzylethers, diglyme, triglyme, diethylene glycol ethyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, propylene glycol phenyl ether, propylene glycol methyl ether, tripropylene glycol methyl ether, toluene, xylene, benzene, dipropylene glycol monomethyl ether acetate, dichlorobenzene, propylene carbonate, naphthalene, diphenyl ether,
20 butyrolactone, dimethylacetamide, dimethylformamide and mixtures thereof.

The concentration of pores in the porous matrix is sufficiently high to lower the dielectric constant of the matrix but sufficiently low to allow the matrix to withstand the process steps required in the manufacture of the desired microelectronic device (for example, an integrated circuit, a multichip module, or a flat panel display device).

25 Preferably, the density of pores is sufficient to lower the dielectric constant of the matrix to less than 2.5, more preferably to less than 2.0. Preferably, the concentration of the pores is at least 5 volume percent, more preferably at least 10 volume percent and most preferably at least 20 volume percent, and preferably not more than 70 volume percent, more preferably not more than 60 volume percent based on the total volume of the porous matrix.

30 The average diameter of the pores is preferably less than 400 nm; more preferably, less than 100 nm; more preferably still, not more than 50 nm; even more preferably, not more than 20 nm; and most preferably, not more than 10 nm.

Methods of Preparing a Porous Matrix Layer

While not being bound by theory, it is thought that the following events occur
35 during the processing of solutions containing a matrix precursor and a poragen. The

solution of matrix precursor and poragen is applied to a substrate by a method such as spin coating. During this application some of the solvent evaporates leaving a more concentrated solution on the substrate. The coated substrate is then heated on a hot plate to remove most of the remaining solvent(s) leaving the poragen dispersed in the matrix precursor. During the solvent removal process and/or during subsequent thermal processing, the poragen phase separates from the matrix precursor. This phase separation may be driven by loss of solvent (concentration effect and/or change in solubility parameter of the solution), increases in molecular weight of the matrix precursor, assembly or aggregation of sufficient poragen mass in a specific location, or combinations thereof. With further heat treatments, the matrix becomes more fully cured. At an elevated temperature the poragen begins to decompose into fragments which can diffuse out of the coated film leaving behind a pore, thus forming a porous matrix.

The matrix precursor, the poragen and a solvent are combined and mixed to form an optically clear solution. The amount of matrix precursor relative to the amount of poragen may be adjusted to give the desired porosity. However, preferably, the weight percent of poragen based on weight of poragen and matrix is at least 5 percent, more preferably at least 10 percent, and most preferably at least 20 percent. The maximum amount of poragen will be determined by the mechanical and electrical properties desired in the final product. Preferably, the weight percent poragen is no greater than 80 percent, more preferably no greater than 70 percent, and most preferably no greater than 60 percent.

Sufficient solvent to provide an optically clear solution should be used. In addition, the amount of solvent may be varied to allow one to get various coating thicknesses. The more solvent that is used, the thinner the layer of the final film. Preferably, the amount of solvent is in the range of 50-95 percent by weight of the total solution.

Any known coating method may be used to apply the precursor/poragen/solvent composition to a substrate. Spin coating is particularly suitable for providing the very thin film layers desired. Preferred film thicknesses are less than 10 microns, preferably less than 5 microns, for interlevel dielectric films. The composition may be applied to any substrate where a thin porous film is desired. Preferably, the substrate comprises a silicon wafer. The substrate may further comprise other layers or features such as are found in integrated circuits, (for example, gates, metal interconnect lines, other insulating materials, etc.).

The solvents used may be any solvent or combination of solvents in which the combination of poragen and matrix precursor forms a solution. Examples of suitable solvents include mesitylene, pyridine, triethylamine, N-methylpyrrolidinone (NMP), methyl benzoate, ethyl benzoate, butyl benzoate, cyclopentanone, cyclohexanone, 5 cycloheptanone, cyclooctanone, cyclohexylpyrrolidinone, and ethers or hydroxy ethers such as dibenzylethers, diglyme, triglyme, diethylene glycol ethyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, propylene glycol phenyl ether, propylene glycol methyl ether, tripropylene glycol methyl ether, toluene, xylene, benzene, dipropylene glycol monomethyl ether acetate, dichlorobenzene, propylene 10 carbonate, naphthalene, diphenyl ether, butyrolactone, dimethylacetamide, dimethylformamide and mixtures thereof.

The poragen and matrix precursor may be simply mixed prior to application or they may be partially reacted or b-staged prior to application of the solution to the desired substrate. The poragen may be added at various stages of the matrix precursor B-staging 15 process as desired.

After the matrix precursor film is formed, the film can be baked under conditions sufficient to remove solvent and cause further polymerization of the matrix precursor. Baking temperature is system dependent and can be determined by one of 20 ordinary skill in the art without undue experimentation. The subsequently formed coating of matrix precursor or matrix material, which is typically 0.1 to 5 microns thick, can be smoothed, if desired, by chemical mechanical polishing (CMP). Poragen can be removed either before or after the CMP process.

A thermal decomposition of the poragen to low molecular weight species that do not leave substantial residue in the matrix is preferred. After applying the composition to 25 the substrate, the solvent is removed; typically, by heating to a moderate temperature. The composition is then heated rapidly to at least a temperature sufficient to cross-link the precursor materials and form the matrix. The poragen is removed by heating to a temperature sufficient to decompose the poragen. When a polystyrene containing poragen is used, it is preferred that the heating occurs in the absence of oxygen. While the drying 30 (solvent removal), curing, and decomposition steps may occur by separate heating steps, it is also possible that a single heating step could be used and it is recognized that even if multiple heating stages are used, more than one of the processes may be occurring in any given heating step.

Preferably, at least 80 percent of the poragen is removed, more preferably at 35 least 90 percent, and most preferably at least 95 percent. Removal of the poragen may be

determined by techniques such as infrared spectroscopy, transmission electron microscopy, etc. Removal of the poragen may occur when the poragen degrades into low molecular weight species that can diffuse from the film. Preferably, at least 80 percent of the poragen degrades into low molecular weight species, more preferably at least 90 percent, and most preferably at least 95 percent. Preferably, at least 80 percent, more preferably at least 90 percent and most preferably at least 95 percent of the thermoplastic poragen degrades into its monomeric units or smaller units.

According to one preferred embodiment, after coating, the coated substrate is heated to a temperature sufficient to cause rapid cure but below the decomposition temperature for the poragen. Suitable methods for performing such a rapid heating step include baking on a hot plate, and rapid thermal anneal under infrared lamps. For the preferred matrix materials, such as those found in WO 98/11149, the composition preferably is raised to a temperature of above 300°C, more preferably 350°C, at a rate of at least 20°C per second, more preferably at least 50°C per second. This initial curing step need not cause complete cure, so long as the matrix is sufficiently cured as to "lock" the structure of the poragen and the matrix. At least one additional heating step is then performed to fully complete the cure, if necessary, and to decompose the poragen. This subsequent heating step preferably occurs at temperatures above 400°C, more preferably above 420°C, and preferably less than 500°C, more preferably less than 470°C.

According to an alternate embodiment, a single rapid heating step at a rate of preferably at least 20°C per second, more preferably at least 50°C per second, to a temperature sufficient to cause both cure and decomposition of the poragen may be used. In this embodiment, either after drying or without using a separate drying step, the temperature is rapidly raised. For the preferred matrix materials, such as those found in WO 98/11149, the temperature is raised to greater than 400°C, and more preferably greater than 420°C.

If multiple layers of the film are desired, the above steps may be repeated. Also, after forming the porous film, that layer may be etched or imaged by known methods to form trenches, vias, or holes, as are desired in manufacture of an integrated circuit article and other microelectronic devices.

The cross-linked hydrocarbon-containing matrix/poragen system is selected such that the matrix forms before the poragen degrades, and the poragen degrades completely or substantially completely before the matrix degrades. It is preferable that the temperature window from cross-linking to degradation of the matrix be wide to have the greatest flexibility in the choice of poragen.

Poragen can be removed by a number of methods including the preferred thermal burnout method discussed above. This thermal burnout may occur in the absence of oxygen or with oxygen present or even added to accelerate the removal of poragen. This second approach is particularly desirable where the thermosetting matrix is comparatively thermo-oxidatively stable. Poragen can also be removed by wet dissolution, wherein the poragen is effectively dissolved away from the thermoset with an appropriate solvent or by dry or plasma removal, wherein plasma chemistry is used to remove the poragen selectively. For example, a solvent or supercritical gas, such as those listed above, can be used to dissolve and remove a dispersed second phase. The second phase may be a thermoplastic material, a diblock polymer, an inorganic material, or any material that can be dispersed on a nanoscale level and is capable of being dissolved in a solvent that can diffuse into and out of a polymer system.

The porous cross-linked matrix of the present invention may be used as one or more of the insulating or dielectric layers in single or multiple layer electrical interconnection architectures for integrated circuits, multichip modules, or flat panel displays. The polymer of the invention may be used as the sole dielectric in these applications, or in conjunction with inorganic dielectrics such as silicon dioxide, silicon nitride, or silicon oxynitride, or with other organic polymers.

The porous hydrocarbon-containing matrix material of the present invention is particularly useful as a low dielectric constant insulating material in the interconnect structure of an integrated circuit, such as those fabricated with silicon or gallium arsenide. The porous hydrocarbon-containing matrix material may also be used in the process for making integrated circuit devices as disclosed in U.S. Patents 5,550,405 and 5,591,677.

The following examples are for illustrative purposes only and are not intended to limit the scope of this invention.

Example 1 – Preparation of a Porous Benzocyclobutene Matrix

Using a Reactive Thermoplastic Oligomer Preparation of Poly(propylene glycol) Biscinnamate

Into a 250 mL round bottom flask equipped with a magnetic stirrer, an equilibrating addition funnel, and a reflux condenser with a nitrogen inlet was added, with stirring, poly(propylene glycol) having a number average molecular weight of 8000 (38.21 g, 4.78 mmol) and chloroform (40 mL). Pyridine (0.60 g, 7.64 mmol) was then added to the stirred solution. Cinnamoyl chloride (0.64 g, 3.82 mmol) was added dropwise to the solution over 15 minutes. Upon completion of addition, the reaction mixture was heated under reflux for 18 hours. The reaction was then cooled to room temperature. The solution was washed

with 10 percent HCl (3 x 25 mL), then water (1 x 50 mL), then 1M NaOH (2 x 25 mL), then water again (1 x 50 mL), then brine (1 x 50 mL). The organics were then dried over magnesium sulfate, and the solvent removed to yield the product (37.5 g) the structure of which was confirmed by proton and carbon NMR spectroscopy.

5 Preparation of a Copolymer Divinylsiloxane-bis-benzocyclobutene and Poly(propylene glycol) Biscinnamate

Into a glass reactor was placed divinylsiloxane-bis-benzocyclobutene (CAS# 124221-30-3) (4.0 g, 1.024×10^{-2} mol) and poly(propylene glycol) biscinnamate (1.0 g, 1.22×10^{-4} mol). The mixture, which formed a single phase, was heated at 200°C for 18 hours, whereupon the material had become white and hard. This material was heated to 325°C under nitrogen for 50 hours to afford a porous article having a pore size (as determined by transmission electron microscopy) in the range of 10 to 50 nm.

Example 2 - Preparation of a Porous Thin Film of a Benzocyclobutene

15 Matrix Using a Reactive Thermoplastic Oligomer

A solution of oligomeric divinylsiloxane-bisbenzocyclobutene, Mw 49600 in mesitylene, 80 parts was combined with 20 parts of the poly(propylene glycol) biscinnamate prepared from poly(propylene glycol) Mw 4000. This solution was heated at 165°C under nitrogen for 4.5 hours to further advance the molecular weight. Upon cooling to room temperature, the total percent solids of the solution was adjusted to 20 percent by addition of the appropriate amount of mesitylene.

Ten milliliters of the above solution was puddled onto a 4 inch (10.16 cm) silicon wafer and first spun at 500 rpm for 3 seconds followed by spinning at 2,000 rpm for 30 seconds. The wafer was then subjected to the following thermal conditions: hot plate for 5 minutes at 200°C; 250°C for 6 minutes; 350°C for 10 minutes. The wafer was transferred to an oven with a nitrogen atmosphere and held at 300°C for 9 hours. Transmission electron microscopy indicated the presence of pores which ranged in size from 20 - 100 nm with an average value of 60-70 nm

Example 3 – Preparation of a Porous Polyarylene Thin Film Using a Reactive Polystyrene Poragen

30 Preparation of 3,5-Bis(phenylethynyl)benzoyl Chloride

a.) Preparation of Methyl 3,5-Dibromobenzoate

To a 250 mL round bottom flask fitted with a condenser and nitrogen inlet were added 3,5-dibromobenzoic acid (30.06 g, 0.1074 mole), methanol (60 g, 1.87 moles), and concentrated sulfuric acid (1.8 mL). The mixture was heated to reflux for 23 hours and the mixture was cooled to room temperature during which time a solid precipitated. The

mixture was cooled in an ice bath and the solid isolated by filtration. The solid was rinsed with cold methanol and then dried in vacuo at 40°C. Reaction and final product were analyzed by GC to monitor reaction progress and assess purity of product.

b.) Coupling of Methyl 3,5-Dibromobenzoate with Phenylacetylene

5 To a 1 L round bottom flask fitted with a nitrogen inlet was added methyl 3,5-dibromobenzoate (26.4 g, 0.08981 mole), palladium chloride bis(triphenylphosphine) (6.258 g, 0.008916 mole), triphenylphosphine (1.18 g, 0.004504 mole), phenylacetylene (27.40 g, 0.2682 mole), triethylamine (36.13 g, 0.3569 mole), and tetrahydrofuran (THF) (500 mL). The mixture was stirred at room temperature for 20 minutes. Copper(I) iodide (0.428 g, 10 0.00225 mole) was then added and the mixture stirred at room temperature for 95 hours. Reaction was followed by GC. Solvent was removed in vacuo. Residue was slurried with methanol and isolated by filtration. Solid was dissolved in methylene chloride and filtered through a plug of silica gel in a filter funnel. Solvent was removed in vacuo to give a brown solid.

15 c.) Preparation of 3,5-Bis(phenylethynyl)benzoic Acid

To a 1 L round bottom flask was added methyl 3,5-bis(phenylethynyl)benzoate (32.7 g, 0.0972 mole) and isopropanol (261 mL). The mixture was heated to reflux until all the solid dissolved. Potassium hydroxide (24.24 g of 45 percent KOH aq., 0.1944 mole) was added and the mixture was kept hot for 4 hours. The 20 mixture was allowed to cool then acidified with concentrated HCl until solid precipitated. The solid was isolated by filtration and dried in vacuo at 80°C overnight giving a grayish solid (22 g). The solid was refluxed in toluene with decolorizing charcoal, filtered hot through filter aid, and cooled during which time a solid precipitated. The solid was isolated by filtration and dried in vacuo overnight. Analysis by high performance liquid 25 chromatography (HPLC) showed the material to be pure. The material was further analyzed by ¹H-NMR and ¹³C-NMR. Spectra were consistent with the desired structure.

d.) Preparation of 3,5-Bis(phenylethynyl)benzoyl Chloride

3,5-Bis(phenylethynyl)benzoic acid (2.7982 g, 0.008680 mole), oxalyl chloride (2.2 mL, 0.02521 mole), and toluene (7 mL) were added to a 50 mL round bottom 30 flask. The mixture was heated at 50°C until all the solid had dissolved plus an additional hour. The solvent and excess oxalyl chloride were removed by applying a vacuum. The solid was redissolved in toluene at room temperature then solvent removed by applying vacuum. Solid was used subsequently without further purification.

Preparation of a Poly(styrene) Ester of 3,5-Bis(phenylethynyl)benzoic Acid

Charged to a 1.5 L glass polymerization reactor, which had been cleaned with refluxing toluene and dried under vacuum, was 700 mL of cyclohexane (passed through activated alumina). The reactor was heated to 55°C and 103.3 g of styrene (passed through activated alumina, distilled from calcium hydride and dibutylmagnesium prior to use) were added. The polymerization was initiated by adding 9.0 mL (3.456 mmol) of 0.384 M *sec*-butyl lithium solution. After stirring for 1 hour, 0.60 g of ethylene oxide (dried over calcium hydride) was added causing the orange color solution to become colorless. After 30 min, 1.778 g (3.456 mmol, 1.0 equivalent) of 3,5-bis(phenylethynyl)benzoyl chloride, in 10 mL of tetrahydrofuran (passed through activated alumina) were added. After 30 minutes, the solution was cooled and removed from the reactor. The polymer was isolated by precipitating it in 1.5 L of methanol and drying it under vacuum at 80°C overnight. The yield was quantitative. GPC analysis, versus narrow molecular weight polystyrene standards, of the polymer gave $M_n=39,353$, $M_w=41,303$ and $M_w/M_n=1.050$. Analogously, functionalized polystyrenes with M_n values of 46,500 and 50,000 were also prepared.

Preparation of Oligomer Solution from 4,4'-Bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl ether, 1,3,5-Tris(phenylethynyl)benzene and Polystyrene Ester of 3,5-Bis(phenylethynyl)benzoic Acid

To a 500 mL 3-necked round bottom flask was added 4,4'-bis(2,4,5-triphenylcyclopentadienone)diphenyl ether (45.38 g, 0.0580 mole), 1,3,5-tris(phenylethynyl)benzene (14.62 g, 0.0386 mole), polystyrene ester of 3,5-bis(phenylethynyl)benzoic acid ($M_n=39,353$) (15.00 g, 0.000375 mole), and gamma-butyrolactone (140 g). The flask was attached to a nitrogen/vacuum inlet. The magnetically stirred solution was degassed by applying vacuum and refilling with nitrogen five times. The solution was then heated to an internal temperature of 200°C. After 55.5 hours of heating, the solution was allowed to cool to 145°C then diluted with cyclohexanone (205 g). The solution was then allowed to cool to room temperature. Analysis of the final solution by gel permeation chromatography indicated a $M_n=5362$ and a $M_w=34022$ relative to a polystyrene standard. Similar solutions using other molecular weight reactive polystyrenes were prepared analogously.

Preparation and Evaluation of Porous Thin Film

A resin solution from 4,4'-bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl ether and 1,3,5-tris(phenylethynyl)benzene containing the polystyrene ester of 3,5-bis(phenylethynyl)benzoic acid ($M_n=46,500$) as the poragen was prepared as described

above. The solution was applied to a silicon wafer and cast by spin-coating to form a 1.16 μ m thick coating. The film was baked on an MTI hot plate at 320°C for 2 minutes under nitrogen and then at 400°C for 10 minutes under nitrogen. The coating on the wafer was further heated at 450°C under nitrogen for 20 minutes in a Blue M oven. The pores were 120 nm in diameter based on visual inspection of a TEM view of the film. The refractive index was 1.58.

Example 4 - Preparation of Porous Polyarylene
Thin Films Using Non-Reactive Polystyrene Poragens

Preparation of Oligomer Solution from 4,4'-Bis(2,4,5-
triphenylcyclopentadien-3-one)diphenyl Ether and
1,3,5-Tris(phenylethynyl)benzene Mole Ratio 3:2

To a 500 mL 3-necked round bottom flask was added 4,4'-bis(2,4,5-triphenylcyclopentadienone)diphenyl ether (60.00 g, 0.07662 mole), 1,3,5-tris(phenylethynyl)benzene (19.34 g, 0.0511 mole), and gamma-butyrolactone (185 g). The flask was attached to a nitrogen/vacuum inlet. The magnetically stirred solution was degassed by applying vacuum and refilling with nitrogen five times. The solution was then heated to an internal temperature of 200°C. After 48 hours of heating, the solution was allowed to cool to 145°C then diluted with cyclohexanone (132 g). The solution was then allowed to cool to room temperature. Analysis of the final solution by gel permeation chromatography indicated a M_n =5550 and a M_w =30550 relative to a polystyrene standard.

Preparation of Anionically Polymerized Polystyrene

Charged to a 1.5 L glass polymerization reactor, which had been cleaned with refluxing cyclohexane and dried under vacuum, was 750 mL of cyclohexane (passed through activated alumina). The reactor was heated to 55°C and 103.22 g of styrene (passed through activated alumina and Q5 catalyst bed) were added. The polymerization was initiated by adding 7.8 mL of 1.32 M *sec*-butyl lithium solution. After stirring for 1 hour, 1 mL of methanol was added to quench the polymerization. The solution was stirred for an additional 30 minutes as the reactor cooled. The polymer was isolated by precipitating it in 2 L of methanol and drying it under vacuum at 90°C overnight. A total of 101.96 g (99 percent yield) were collected. GPC analysis, versus narrow molecular weight polystyrene standards, of the polymer gave M_n =8,296, M_w =8,679 and M_w/M_n =1.046. Other molecular weights of polystyrene were prepared analogously.

Preparation of Hydroxy Terminated
Anionically Polymerized Polystyrene

Charged to a 1 L one-neck round-bottom flask, equipped with magnetic stirring bar, septum port with septum, and a nitrogen inlet adapter, was 208 g of

cyclohexane (passed through activated alumina) and 52.64 g of styrene (passed through activated alumina, distilled from calcium hydride and dibutyl magnesium). The polymerization was initiated at room temperature by adding 5.6 mL of 0.624 M *sec*-butyl lithium solution resulting in an orange colored solution. After 2 hours, 2.31 g of ethylene oxide (dried over calcium hydride) were added to give a colorless solution. After 30 minutes, 2 mL of methanol (MeOH) were added to terminate the polymerization. The polymer was isolated by precipitating it in MeOH and drying under vacuum at 90°C overnight. The yield was quantitative. GPC analysis, versus narrow molecular weight polystyrene standards, gave $M_n=14,960$, $M_w=16,035$ and $M_w/M_n=1.072$. Other molecular weights of hydroxy terminated polystyrene were prepared analogously.

Preparation of a Star Polystyrene

To a 250 mL round bottom flask fitted with a Dean Stark trap/condenser/nitrogen inlet was added hydroxy terminated polystyrene ($M_n=4837$) (10.00 g, 0.0207 mole) and toluene (150 mL). The mixture was stirred until the solid had dissolved. The mixture was heated to reflux for 2 hours to remove any water azeotropically. The solution was allowed to cool to room temperature then the flask was sealed with a rubber septum. Silicon tetrachloride (59 microliters, 0.000517 mole) was added via syringe and the mixture stirred for 5 minutes. Pyridine (50 microliters) was added via syringe and the mixture stirred for 48 hours at room temperature. The mixture was then heated to reflux for 1.5 hours. The solvent was then removed in vacuo. The residue was dissolved in methylene chloride, washed with HCl(aq.), and NaCl(sat.), then dried ($MgSO_4$) and solvent removed in vacuo. Analysis of the material by gel permeation chromatography indicated a $M_n=16876$ and a $M_w=17222$ relative to polystyrene standards.

Formulation, Thin Film Formation, and Evaluation Using 8700 M_n Polystyrene

Anionically polymerized polystyrene with a M_n of 8700 was added, 20 percent by mass relative to solids, to the oligomer solution from 4,4'-bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl ether and 1,3,5-tris(phenylethynyl)benzene mole ratio 3:2 prepared as described above. The solution was optically transparent with a dark red cast indicating dissolution of the polystyrene into the b-staged resin. The solution was applied to a silicon wafer and cast by spin-coating to form a 3.5 μm thick coating. The film was baked on an MTI hot plate at 320°C for 2 minutes under nitrogen and then at 400°C for 10 minutes under nitrogen. The coating on the wafer was further heated at 425°C under nitrogen for 60 minutes in a Blue M oven. After this latter heating step, 95 percent of the polystyrene was determined by fourier transform infrared spectroscopy (FTIR) to have been removed. An estimate of the average pore size

based on visual inspection of a TEM view of the film was 300 nm. The index of refraction of the porous coating was 1.5; this compares to an index of refraction of 1.63 for the fully dense matrix.

The solution containing polystyrene from above was applied to a silicon wafer and cast by spin-coating to form a 3.3 μm thick coating. The film was baked on a hot plate at 380°C for 2 minutes under nitrogen and then at 400°C for 10 minutes under nitrogen. The coating on the wafer was then heated in an oven at 425°C under nitrogen for 6 minutes. The latter heating step removed 80 percent of the polystyrene as measured by FTIR. The estimated average pore size was 30 nm. Subsequent heating at 450°C for 20 minutes removed most of the remaining polystyrene. The pore morphology was essentially unchanged with an average pore size of 30 nm.

The solution containing polystyrene from above was applied to a silicon wafer and cast by spin-coating to form a 5.8 μm thick coating. The film was baked on an MTI hot plate at 340°C for 2 minutes under nitrogen and then at 400°C for 10 minutes under nitrogen. The coating on the wafer was further heated at 425°C under nitrogen for 60 minutes in a Blue M oven. An estimate of the average pore size, based on visual inspection of a TEM view of the film, was 300 nm.

Formulation, Thin Film Formation, and Evaluation Using 15,800 M_n Polystyrene

Anionically polymerized polystyrene with a M_n of 15,800, as purchased from Scientific Polymer Products Inc., was added (20 percent by mass relative to solids) to the oligomer solution from 4,4'-bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl ether and 1,3,5-tris(phenylethynyl)benzene mole ratio 3:2 prepared as described above. Mesitylene was added so that the total solids content was 20 percent. The solution was applied to a silicon wafer and cast by spin-coating to form a 1.85 μm thick coating. The film was baked on a hot plate at 320°C for 2 minutes under nitrogen and then at 400°C for 10 minutes under nitrogen. The coating on the wafer was then heated in an oven at 450°C under nitrogen for 20 minutes. The estimated average pore size was 200 nm. The volume fraction was measured to be between 11 percent and 15 percent using image analysis of the TEM micrographs. The dielectric constant measured with a 0.25 inch (.635 cm) diameter parallel plate capacitor was 2.3.

Formulation, Thin Film Formation, and Evaluation Using 12,400 M_n Polystyrene

Anionically polymerized polystyrene with a M_n of 12,400 M_n as purchased from Scientific Polymer Products Inc., was added (20 percent by mass relative to solids) to

the oligomer solution from 4,4'-bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl ether and 1,3,5-tris(phenylethynyl)benzene mole ratio 3:2 prepared as described above. The total solids content was adjusted to 15 percent with cyclohexanone. The solution was applied to four nearly identical 200 mm silicon wafers and cast by spin-coating on a MTI 200 mm track coater to form a 0.9 μm thick coating. The films were baked on a hot plate on the track at 150°C for 2 minutes under nitrogen. Subsequently, two of the films were baked at 320°C under a 7 psi nitrogen purge on a hot plate module contiguous to the track coater. The remaining wafers were baked at 320°C under a 55 psi nitrogen purge on a stand-alone module hot plate similar to the hot plate contiguous to the track. All four films were then baked at 400°C for 10 minutes under the 55 psi nitrogen purge and, finally, heated in an oven at 450°C under nitrogen for 20 minutes to remove the polystyrene. The wafers baked at 320°C on the 7 psi nitrogen purge hot plate suffered film loss proportional to the poragen content with the final thickness of 0.68 μm and refractive index of 1.63; indicating film collapse in lieu of pore formation. The wafers baked under the 55 psi purge had a final thickness of 0.83 μm and a refractive index of 1.55; indicative of pore formation during the 450°C heating step.

Formulation, Thin Film Formation, and Evaluation of Star Polystyrene in Oligomer Solution from 4,4'-Bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl Ether and 1,3,5-Tris(phenylethynyl)benzene Mole Ratio 3:2

The star polystyrene material from above was added at a 20 weight percent level, relative to solids, to the oligomer solution from 4,4'-bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl ether and 1,3,5-tris(phenylethynyl)benzene mole ratio 3:2 described above. The solution was applied to a silicon wafer and cast by spin-coating to form a 2.2 μm thick coating. The film was baked on an MTI hot plate at 320°C for 2 minutes under nitrogen and then at 400°C for 10 minutes under nitrogen. The coating on the wafer was further heated at 425°C under nitrogen for 60 minutes in a Blue M oven. An estimate of the average pore size based on visual inspection of a TEM view of the film was 120 nm. The index of refraction of the porous coating was 1.56.

Example 5 - Preparation of a Porous Polyarylene Thin Film Using a Reactive Polyamide Poragen

Preparation of Polyamide from Sebacoyl Dichloride and 2,5-Dimethylpiperazine

To a 1 L round bottom flask was added 2,5-dimethylpiperazine (recrystallized from acetone) (10.0000 g, 0.08757 mole) and chloroform (400 mL). Triethylamine (23.1 mL, 0.1656 mole) was added via syringe. Sebacoyl chloride (19.799 g, 0.08279 mole) was

weighed into a beaker, dissolved in chloroform (300 mL), and transferred to a dropping funnel attached to the 1 L round bottom flask. The solution of acid chloride was added quickly to the solution of diamine. The dropping funnel was rinsed with chloroform (50 mL) which was added to the reaction mixture. The mixture was stirred at room temperature for 5 10 minutes. The mixture was then poured into hexanes (2 L) precipitating a white solid. Water (1 L) was added and the mixture stirred. The liquid layer was decanted from the white solid. The solid was taken up in chloroform and the top aqueous layer was removed and discarded. Solvent was removed in vacuo. The residue was taken up in dimethylformamide and then precipitated into water. The resultant solid was isolated by 10 filtration and dried in vacuo at 100°C overnight.

Reaction of Polyamide from Sebacoyl Dichloride and 2,5-Dimethylpiperazine with 3,5-Bis(phenylethynyl)-benzoyl Chloride

3,5-Bis(phenylethynyl)benzoic acid (0.3224 g, 0.001 mole) was weighed into 15 a 25 mL round bottom flask. Thionyl chloride (10 mL) was added and the mixture stirred for 2 hours at room temperature. The excess thionyl chloride was removed by distillation then by application of vacuum. The resultant solid was dissolved in chloroform and the solvent removed in vacuo twice. The solid was then dissolved in chloroform. The polyamide prepared as described above (5.0 g, 0.0005 mole) was weighed into a 100 mL round 20 bottom flask and dissolved in chloroform (50 mL). The solution of acid chloride was then added followed by triethylamine (0.5 mL). The mixture was stirred at room temperature for 17 hours. The reaction mixture was filtered through a 1 micron filter then diluted with hexanes precipitating a light yellow solid. Solvent was decanted from the solid and additional hexanes were added. The solvent was again decanted off and the solid dried in 25 vacuo at room temperature. A sample was analyzed by gel permeation chromatography which indicated a $M_n=24100$ and a $M_w=43803$.

Preparation of Oligomer Solution from 4,4'-Bis(2,4,5-triphenyl-cyclopentadien-3-one)-diphenyl Ether, 1,3,5-Tris(phenylethynyl)benzene and Polyamide Endcapped with 3,5-Bis(phenylethynyl)benzamide Groups

To a 500 mL 3-necked round bottom flask was added 4,4'-bis(2,4,5- 35 triphenylcyclopentadienone)diphenyl ether (10.0000 g, 0.01277 mole), 1,3,5-tris(phenylethynyl)benzene (4.8340 g, 0.01277 mole), polyamide endcapped with 3,5-bis(phenylethynyl)benzamide groups from above (3.7085 g, 0.000154 mole), and gamma-butyrolactone (43.27 g). The flask was attached to a nitrogen/vacuum inlet. The magnetically stirred solution was degassed by applying vacuum and refilling with nitrogen five times. The solution was then heated to an internal temperature of 200°C. After 48 hours of heating, the

solution was allowed to cool to 145°C then diluted with cyclohexanone (30.89 g). The solution was then allowed to cool to room temperature. Analysis of the final solution by gel permeation chromatography indicated a M_n =5071 and a M_w =14378 relative to a polystyrene standard. The solution was applied to a silicon wafer and cast by spin-coating to form a 1.5 μ m thick coating.

- 5 The film was baked on an MTI hot plate at 320°C for 2 minutes under nitrogen and then at 400°C for 10 minutes under nitrogen. The coating on the wafer was further heated at 450°C under nitrogen for 20 minutes in a Blue M oven. The pore sizes based on visual inspection of a TEM view of the film appeared to be bimodal with larger pores of 250 nm diameter and smaller pores of 30 nm.

10 Example 6 - Preparation of a Porous Polyarylene
Thin Film Using Latex Particles as Poragens

Formulation of Latex Particles in Oligomer
Solution from 4,4'-Bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl Ether and 1,3,5-Tris-
15 (phenylethynyl)benzene Mole Ratio 3:2

- Cross-linked latex solutions (such as those available from the Dow Chemical Company) were added at a 20 weight percent level, on a solids to solids basis, to the oligomer solution from 4,4'-bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl ether and 1,3,5-tris(phenylethynyl)benzene mole ratio 3:2 described above, which had been
- 20 precipitated into water, dried, and redissolved in Dowanol PM Acetate. The solutions were heated to reflux in a round bottom flask fitted with a Dean Stark trap/condenser/nitrogen inlet to remove the water introduced with the latex particles by azeotropic distillation. The resultant solutions were cooled and then used in subsequent processing. A resin solution containing DW-110NA latex (from The Dow Chemical Company) as the poragen was
- 25 prepared as described. The solution was applied to a silicon wafer and cast by spin-coating to form a 2.7 μ m thick coating. The film was baked on an MTI hot plate at 320°C for 2 minutes under nitrogen and then at 400°C for 10 minutes under nitrogen. The coating on the wafer was further heated at 450°C under nitrogen for 20 minutes in a Blue M oven. The pores appeared to be oblate with the long axes in the plane of the film based on visual
- 30 inspection of a TEM view of the film. The long axes were 150 nm diameter and short axis was 50 nm.

Example 7 - Preparation of a Porous Polyarylene
Thin Film Using a Dendritic Polyester as Poragen

Preparation of Boltron H40 Benzoate

- 35 Into a 250 mL round bottom flask equipped with a magnetic stirrer, equilibrating addition funnel, and a reflux condenser with a nitrogen inlet was added, with

stirring, Boltron H40 dendritic polyester polymer having a theoretical molecular weight of 7,316 g permole (5.0 g, 8.75 mmole OH per g, 44 mmole) and THF (70 mL). Pyridine (7 mL) was then added to the stirred solution. Benzoyl chloride (7.03 g, 50 mmol) was added dropwise to the solution over 15 minutes. Upon completion of addition, the reaction mixture
5 was heated under reflux for 2 hours. The reaction was then cooled to room temperature. The solution was filtered, diluted with 200 mL of methylene chloride, washed with 10 percent HCl (3 x 25 mL), then water (1 x 50 mL), then 1 M NaOH (2 x 25 mL), then water again (1 x 50 mL), and then brine (1 x 50 mL). The organics were then dried over magnesium sulfate, and the solvent removed to yield the crude product, which was further
10 purified by precipitation into methanol to afford 7.4 g product (77 percent); the structure of which was confirmed by proton and carbon NMR spectroscopy.

Synthesis of 1,2,3,4-Tetrakis(phenylethynyl)benzene

In a 250 mL flask was placed 11.81 g (0.030 mole) of 1,2,3,4-tetrabromobenzene (Collins, I., Suschitzky, H., *J. Chem. Soc., C*, **1969**, 2337), 27.0 g (0.267
15 mole) of triethylamine, 13.6 g (0.132 mole) of phenylacetylene, and 60 mL of N, N-dimethyl formamide. The reaction mixture was purged with nitrogen for 15 minutes and then 0.945 g (0.0036 mole) of triphenylphosphine and 0.135 g (0.0006 mole) of palladium acetate were added. After heating the reaction mixture at 80°C under nitrogen atmosphere for 20 hours, the flask was allowed to cool to room temperature, water (100 mL) and toluene (100 mL) were
20 added. The resulting organic layer was washed with 10 percent HCl, water and saturated NaCl and dried with Na₂SO₄. The pure product (5.4g, 38 percent) was obtained upon removal of the solvent and recrystallization from hexane/toluene mixture. ¹H NMR (CDCl₃, 300 MHz) δ 7.37 (m, 12H), 7.50 (s, 2H), 7.62 (m, 8H). ¹³C NMR (CDCl₃, 75 MHz) δ 87.3, 88.1, 95.5, 98.2, 123.1, 123.4, 125.7, 128.4, 128.5, 128.8, 130.9, 131.8, 131.9.

25 Formulation, Thin Film Formation, and Evaluation of Boltron H40 Benzoate + 1,2,3,4-Tetrakis(phenyl-ethynyl)benzene in Oligomer Solution from 4,4'-Bis-(2,4,5-triphenylcyclopentadien-3-one)diphenyl Ether and 1,3,5-Tris(phenylethynyl)benzene Mole Ratio 1:1

30 Boltron H40 Benzoate as prepared above, 25 percent by mass relative to solids, and 1,2,3,4-tetrakis(phenylethynyl)benzene, 20 percent by mass relative to solids, were added to the oligomer solution from 4,4'-bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl ether and 1,3,5-tris(phenylethynyl)benzene mole ratio 1:1 in gamma-butyrolactone and cyclohexanone as described in WO 98/11149. The solution was optically
35 transparent with a dark red cast indicating dissolution of the Boltron H40 Benzoate and 1,2,3,4-tetrakis(phenylethynyl)benzene into the b-staged resin. The solution was applied to

a silicon wafer and cast by spin-coating to form a 1.6 μm thick coating. The film was baked on an MTI hot plate at 320°C for 2 minutes under nitrogen and then at 400°C for 10 minutes under nitrogen. The coating on the wafer was further heated at 425°C under nitrogen for 60 minutes in a Blue M oven. An estimate of the average pore size based on visual inspection
5 of a TEM view of the film was 300 nm. Also, smaller pore structure was apparent with sizes between 5 nm to 10 nm.

Example 8 - Preparation of a Porous Polyarylene
Thin Film Using Block Copolymers as Poragens

Preparation of Poly(styrene-block-methyl
methacrylate) (PS-b-PMMA)

10 Charged to a 500 mL one-neck round bottom flask, equipped with magnetic stirring bar, septum port with septum, and an addition funnel with septum and nitrogen inlet, was 193 g of tetrahydrofuran (passed through activated alumina). The flask was cooled to -78°C and 12.73 g of styrene (passed through activated alumina and Q5 catalyst bed) were
15 added. The polymerization was initiated by adding 1.15 mL (0.84 mmole) of 0.733 M *sec*-butyl lithium solution resulting in an orange colored solution. After 2 hours, the poly(styrene) (PS) block was sampled by removing an aliquot and adding it to methanol (MeOH), and 0.19 g (1.05 mmoles, 1.25 equivalent) of diphenylethylene (distilled from diphenylhexyl lithium) were added to give a dark red color. After 25 minutes, 13.18 g of
20 methyl methacrylate (MMA) (distilled from calcium hydride and triethyl aluminum) were added dropwise via the addition funnel over a 20 minute period. The red color dissipated after the first several drops of MMA. After 1 hour, the polymerization was terminated by adding 0.2 mL of MeOH. The solution was allowed to warm to room temperature and the polymer was isolated by precipitating it in 600 mL of MeOH and collecting it by filtration.
25 Both polymers were dried under vacuum at 60°C for several hours. A total of 24.69 g (95 percent yield) of PS-b-PMMA were collected. GPC analysis, versus narrow molecular weight polystyrene standards, of the PS block gave $M_n=14,567$, $M_w=15,821$ and $M_w/M_n=1.086$; the PS-b-PMMA copolymer gave $M_n=26,825$, $M_w=28,893$ and $M_w/M_n=1.077$. NMR analysis of the block copolymer showed the PMMA block to have $M_n=15,364$ giving
30 $M_n=29,913$ for the copolymer.

Preparation of Poly(butadiene-block- ϵ -caprolactone) (PB-b-PCL)

Charged to a 1.5 L glass polymerization reactor, which had been cleaned with refluxing toluene and dried under vacuum, was 650 mL of cyclohexane (passed through activated alumina). The reactor was heated to 50°C and 32.55 g of 1,3-butadiene
35 (passed through activated alumina and Q5 catalyst bed) were added. The polymerization was initiated by adding 7.0 mL (9.1 mmoles) of 1.3 M *sec*-butyl lithium solution. After

stirring for 2.5 hours, the poly(butadiene) (PB) block was sampled, by removing an aliquot and adding it to methanol (MeOH), and 1.58 g of (3.59 mmol, 3.9 equivalent) of ethylene oxide (dried over calcium hydride) were added. The reactor temperature was increased to 70°C. After 20 minutes, 9.1 mL (9.1 mmol, 1.0 equivalent) of 1.0 M diethylaluminum chloride and 0.1 mL of tetrahydrofuran (passed through activated alumina) were added to give a turbid solution. The reactor was cooled to 60°C and 34.81 g of ϵ -caprolactone (distilled from calcium hydride twice) were added to give a milky solution. After 90 minutes, 0.5 mL of MeOH were added to terminate the polymerization. The solution was stirred for an additional 30 minutes to assure complete termination and then was added to 0.75 g of 2,6-di-*tert*-butyl-4-methyl phenol. The polymer was isolated by precipitating it in 1.2 L of methanol and drying it under vacuum at 50°C for several hours. A total of 48.1 g (71 percent yield) of PB-b-PCL were collected. GPC analysis, versus narrow molecular weight poly(butadiene) standards, of the PB block gave $M_n=4,890$, $M_w=5,080$ and $M_w/M_n=1.039$; the PB-b-PCL copolymer gave $M_n=5,655$, $M_w=6,629$ and $M_w/M_n=1.172$. NMR analysis of the block copolymer showed the PCL block to have $M_n=4,794$ giving $M_n=9,685$ for the copolymer.

Formulation, Thin Film Formation, and Evaluation of Poly(styrene-block-methyl methacrylate) (PS-b-PMMA) in Oligomer Solution from 4,4'-Bis(2,4,5-triphenylcyclopentadien-3-one)-diphenyl Ether and 1,3,5-Tris(phenylethynyl)benzene Mole Ratio 3:2

The block copolymer of polystyrene and PMMA as described above was added (20 percent by mass relative to solids) to the oligomer solution from 4,4'-bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl ether and 1,3,5-tris(phenylethynyl)benzene mole ratio 3:2 described above. The solution was optically transparent with a dark red cast indicating dissolution of the block copolymer into the b-staged resin. The solution was applied to a silicon wafer and cast by spin-coating to form a 1.94 μm thick coating. The film was baked on a MTI hot plate at 400°C for 10 minutes under nitrogen. The coating on the wafer was further heated at 450°C under nitrogen for 20 minutes in a Blue M oven. An estimate of the average pore size based on visual inspection of a TEM view of the film was 200 nm.

Formulation, Thin Film Formation, and Evaluation of Poly(butadiene-block- ϵ -caprolactone) (PB-b-PCL) in Oligomer Solution from 4,4'-Bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl Ether and 1,3,5-Tris(phenylethynyl)benzene Mole Ratio 3:2

The block copolymer of polystyrene and polycaprolactone described above (was added, 20 percent by mass relative to solids) to the oligomer solution from 4,4'-

bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl ether and 1,3,5-tris(phenylethynyl)benzene mole ratio 3:2 described above. The solution was optically transparent with a dark red cast indicating dissolution of the block copolymer into the b-staged resin. The solution was applied to a silicon wafer and cast by spin-coating to form a 2.85 μm thick coating. The film was baked on a MTI hot plate at 320°C for 2 minutes under nitrogen and then at 400°C for 10 minutes under nitrogen. The coating on the wafer was further heated at 450°C under nitrogen for 20 minutes in a Blue M oven. An estimate of the average pore size based on visual inspection of a TEM view of the film was 20 nm.

10 Example 9 - Preparation of a Porous Benzocyclobutene Film Using a Functionalized Dendrimer as Poragen

A polyamidoamine dendrimer, generation 2, available from Dendritech, Inc., was functionalized with phenylpropionic acid to afford a dendrimer with 16 phenylpropiolamides at the periphery. The functionalized propiolamide (0.3 g) was added to 6.0 g of a solution of 25 weight percent oligomeric divinylsiloxane-bis-benzocyclobutene in N-cyclohexylpyrrolidinone. The mixture was warmed to 60°C and then cooled to room temperature and allowed to stand for 48 hours. The weight ratio of dendrimer to benzocyclobutene oligomer was 16.7:83.3 and the total percent solids was 28.6 percent. The prepolymer solution was further diluted with 2.7g of N-cyclohexylpyrrolidinone to afford a final solution of 20 weight percent solids. This solution was spun onto a 4 inch (10.16 cm) silicon wafer (3 seconds per 500 rpm, then 30 seconds per 2000 rpm) and then subjected to the following thermal treatment: 5 minutes per 200°C; 6 minutes per 250°C; hot plate 10 minutes per 350°C and oven 9 hours per 300°C. The film was slightly hazy and when looked at by transmission electron microscopy (TEM) showed a distribution of spherical, closed cell pores ranging in diameter from 5 – 200 nm.

25 Example 10 - Preparation of a Porous Polyarylene Thin Film Using a Non-reactive Star Polyethylene Glycol as Poragen

Preparation of 8 Arm Poly(ethylene glycol) Benzoate

Into a 250 mL round bottom flask equipped with a magnetic stirrer, equilibrating addition funnel, and a reflux condenser with a nitrogen inlet was added, with stirring, branched PEG (8 arms, from Shearwater Polymers) polymer having a molecular weight of 10,000 g per mole (5.0 g, 4 mmole OH) and methylene chloride (40 mL). Triethylamine (5 mL) was then added to the stirred solution. Benzoyl chloride (1.69 g, 12 mmole) in 20 mL methylene chloride was added dropwise to the solution over 15 minutes. Upon completion of addition, the reaction mixture was heated under reflux for 2 hours. The reaction was then cooled to room temperature. The solution was washed with 10 percent

HCl (3 x 25 mL), then water (1 x 50 mL), then 1 M NaOH (2 x 25 mL), then water again (1 x 50 mL), then brine (1 x 50 mL). The organics were then dried over magnesium sulfate, and the solvent removed to yield the crude product, which was further purified by precipitation into ether to afford 4.4 g of product (81 percent). The structure of which was confirmed by proton and carbon NMR spectroscopy.

Formulation, Thin Film Formation, and Evaluation
of 8-Arm Star Poly(ethylene glycol) Benzoate
in Oligomer Solution from 4,4'-Bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl Ether and 1,3,5-Tris(phenylethynyl) benzene Mole Ratio 3:2

The 8-arm star poly(ethylene glycol) benzoate described above, was added, 20 percent by mass relative to solids, to the oligomer solution from 4,4'-bis(2,4,5-triphenylcyclopentadien-3-one)diphenyl ether and 1,3,5-tris(phenylethynyl)benzene mole ratio 3:2 described above. The solution was optically transparent with a dark red cast indicating dissolution of the poragen into the b-staged resin. The solution was applied to a silicon wafer and cast by spin-coating to form a 2.5 μm thick coating. The film was baked on a MTI hot plate at 400°C for 2 minutes under nitrogen and then coating on the wafer was further heated at 450°C under nitrogen for 20 minutes in a Blue M oven. An estimate of the average pore size based on visual inspection of a TEM view of the film was 180 nm.

Example 11 - Preparation of a Porous Polyarylene
Thin Film Using a Polystyrene-*block*-polyarylene

Preparation of Polystyrene Ester of
4-Phenylethynylbenzoic Acid

Into a 250 mL round bottom flask equipped with a magnetic stirrer, an equilibrating addition funnel, and a reflux condenser with a nitrogen inlet was added, with stirring, polystyrene, monohydroxyl terminated polystyrene (from Scientific Polymer Products) having a molecular weight of 10,000 g per mole (10.0 g, 1.0 mmole) and THF (50 mL). Pyridine (5 mL) was then added to the stirred solution. 4-Phenylethynylbenzoyl chloride (0.96 g, 4 mmol) in 10 ml THF was added dropwise to the solution over 15 minutes. The reaction mixture was heated under reflux for 2 hours and then cooled to room temperature. The solution was filtered, diluted with 200 mL of chloroform and washed with 10 percent HCl (25 mL), then water (50 mL), then 1 M NaOH (25 mL), then water again (50 mL), and then brine (50 mL). The organics were then dried over magnesium sulfate and the solvent removed to yield the crude product, which was further purified by precipitation into methanol to afford 9.3 g of product.

Preparation and Thin Film Formulation and Evaluation
of Oligomer Solution from 4,4'-Bis(2,4,5-triphenylcyclopentadien-3-one)-
diphenyl ether, 1,3,5-Tris(phenylethynyl)benzene and Polystyrene
Ester of 4-Phenylethynylbenzoic Acid

5 To a 250 mL 3-necked round bottom flask was added 4,4'-bis(2,4,5-
triphenylcyclopentadienone)diphenyl ether (8.0 g, 0.0102 mole), 1,3,5-tris(phenylethynyl)-
benzene (3.71 g, 0.0098 mole), polystyrene ester of 4-phenylethynyl benzoic acid
(M_w =10,000 g per mole) (3.0 g, 20 percent relative to other solids), and gamma-
butyrolactone (37.3 g). The flask was attached to a nitrogen/vacuum inlet. The
10 magnetically stirred solution was degassed by applying vacuum and refilling with nitrogen
five times. The solution was then heated to an internal temperature of 200°C. After 46
hours of heating, the solution was allowed to cool to 145°C then diluted with cyclohexanone
(19.6 g). The solution was then allowed to cool to room temperature. The solution was
applied to a silicon wafer and cast by spin-coating to form a 4.7 μ m thick coating. The film
15 was baked on a MTI hot plate at 320°C for 2 minutes under nitrogen and then at 400°C for
10 minutes under nitrogen. The coating on the wafer was further heated at 425°C under
nitrogen for 60 minutes in a Blue M oven. An estimate of the average pore size based on
visual inspection of a TEM view of the film was 110 nm.

Example 12 - Preparation of a Porous Perfluorocyclobutane
Thermoset Thin Film Using a Gel-Swell-Cure Procedure

20 In this example, we used an oligomeric solution of perfluorocyclobutene resin
dissolved in mesitylene. The resin was spun coated onto 4 inch (10.16 cm) silicon wafers at
3000 rpm's such that the thickness was near 1 micron. The resin was then reacted to past its
gel point by placing the wafers in an oven which was idling at 161°C; the oven ramped to
25 175°C in 5 minutes and then held at 175°C for 46 minutes. After cooling to room temperature,
the wafers were exposed to either no swelling solution; a solution of 90 percent mesitylene and
10 percent styryl-benzocyclobutene by weight; or a solution of a solution of 90 percent
mesitylene and 10 percent styryl-benzocyclobutene by weight. The exposure was done by
puddling the solution onto the wafer for 1 minute in order to swell the network. The wafer was
30 then spun at 3000 rpms for 45 seconds to remove excess solvent. After spinning, the wafer
was placed onto a hot plate under nitrogen purge for 1 minute at 325°C to cure the film.
Wafers were sampled at various points in the above process and the index of refraction was
measured using ellipsometry at five different points and then averaged. The results are listed
in the table below.

35

Table of Results for Gel-Swell-Cure Experiments

Wafer	Process Sequence	Swell Solution	Index of Refraction
1	Gel	None	1.547 \pm 0.009
2	Gel+Cure (no swell)	None	1.521 \pm 0.006
3	Gel+Swell+Cure	10% styryl-BCB	1.490 \pm 0.004
4	Gel+Swell+Cure	25% styryl-BCB	1.447 \pm 0.019

CLAIMS:

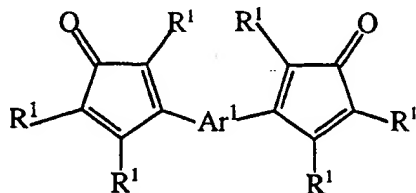
1. A composition comprising: a) a hydrocarbon-containing matrix precursor; and b) a poragen wherein the matrix precursor is selected to form upon curing a cross-linked, hydrocarbon-containing material having a T_g of greater than 300°C

2. The composition of Claim 1 wherein the cross-linked, hydrocarbon-containing material has a thermal stability of at least 400°C.

3. The composition of Claim 1 wherein the matrix precursor comprises a compound selected from benzocyclobutenes; b-staged products of benzocyclobutene; a mixture of polycyclopentadienone functional compounds and polyacetylene functional compounds, at least some of which have three or more reactive functional groups; b-staged products of a mixture of polycyclopentadienones and polyacetylenes, at least some of which have three or more reactive functional groups; perfluoroethylene compounds having a functionality of three or more; a b-staged product of perfluoroethylene compounds having a functionality of three or more; bis-ortho-diacetylene aromatic compounds; and a b-staged reaction product of bis-ortho-diacetylene aromatic compounds.

4. The composition of Claim 3 wherein the matrix precursor comprises a b-staged reaction product of divinylsiloxane-bis-benzocyclobutene.

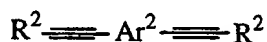
5. The composition of Claim 3 wherein the matrix precursor comprises the partially polymerized reaction products of reactants comprising: (a) a bicyclopentadienone of the formula:



(b) a polyfunctional acetylene of the formula:



(c) and, optionally, a diacetylene of the formula:



wherein R^1 and R^2 are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar^1 , Ar^2 and Ar^3 are independently an unsubstituted aromatic moiety, or inertly-substituted aromatic moiety, and y is an integer of three or more.

6. The composition of Claim 1 wherein the poragen is a polymer.

7. The composition of Claim 2 wherein the poragen is a polymer which degrades at temperatures below the thermal stability temperature of the cross-linked hydrocarbon-containing material.

8. The composition of Claim 6 wherein the poragen is a block copolymer.

5 9. The composition of Claim 7 wherein the poragen is a homopolymer.

10. The composition of Claim 9 wherein the poragen is polystyrene and the cross-linked hydrocarbon-containing material is a polyarylene.

11. The composition of Claim 1 wherein the poragen reacts with the matrix precursor to form groups that are pendant from the cross-linked hydrocarbon-containing material.

12. The composition of Claim 1 wherein the poragen is a particle having an average diameter of 1 to 50 nm, said particle being selected from dendrimers, hyper-branched polymers, and latex particles.

13. The composition of Claim 1 which has a T_g of at least 350°C wherein the poragen is a reactive or non-reactive: a) diblock polymer, wherein one of the blocks is compatible with cross-linked polymer matrix resin and the other block is incompatible therewith; b) dendrimer; c) latex particle; d) solvent; e) gas; f) thermoplastic oligomer or g) material that can be dissolved in a solvent or supercritical gas.

14. The composition of Claim 1 further comprising a solvent.

15. The composition of Claim 14 wherein the solvent is selected from mesitylene, pyridine, triethylamine, N-methylpyrrolidinone (NMP), methyl benzoate, ethyl benzoate, butyl benzoate, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, cyclohexylpyrrolidinone, and ethers or hydroxy ethers such as dibenzylethers, diglyme, triglyme, diethylene glycol ethyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, propylene glycol phenyl ether, propylene glycol methyl ether, tripropylene glycol methyl ether, toluene, xylene, benzene, dipropylene glycol monomethyl ether acetate, dichlorobenzene, propylene carbonate, naphthalene, diphenyl ether, butyrolactone, dimethylacetamide, dimethylformamide and mixtures thereof.

16. The composition of Claim 4 wherein the poragen is selected from poly(alkylene glycol), in which the alkylene group has 2 to 5 carbon atoms, block copolymers of polyalkylene glycols, polyamidoamine dendrimers, and polycaprolactones.

17. The composition of Claim 5 wherein the poragen is selected from reactive and non-reactive polystyrene containing polymers, hyperbranched polyesters, cross-linked polystyrene containing latexes, aliphatic polyamides, polyalkylene glycol-

containing polymers wherein the alkylene group has 2 to 5 carbon atoms, block copolymers of styrene and acrylates or methacrylates, and block copolymers of butadiene and caprolactones.

5 18. A method of making a porous film on a substrate comprising:
providing a substrate;
coating on the substrate a solution comprising the composition of Claim 2 and
a solvent;
removing the solvent, curing the matrix precursor to form the cross-linked
hydrocarbon containing material and degrading the poragen by heating to a temperature
10 less than the thermal stability temperature of the cross-linked hydrocarbon containing
material.

19. The method of Claim 21 wherein the removing, reacting and degrading
steps occur during a single heating step.

15 20. The method of Claim 21 wherein the degrading step comprises removing
at least 80 percent of the thermoplastic from the coating.

21. The method of Claim 21 wherein the cross-linked hydrocarbon-
containing material is a polyarylene and the poragen is polystyrene.

22. A method of making a porous film on a substrate comprising:
providing a substrate;
20 coating on the substrate a solution comprising the composition of Claim 16
and a solvent;
removing the solvent, curing the matrix precursor to form the cross-linked
hydrocarbon-containing material and degrading the poragen by heating.

23. A method of making a porous film on a substrate comprising:
25 providing a substrate
coating on the substrate a solution comprising the composition of Claim 16
and a solvent;
removing the solvent, curing the matrix precursor to form the cross-linked
hydrocarbon-containing material and degrading the poragen by heating.

30 24. A low dielectric constant material comprising a porous cross-linked
hydrocarbon-containing matrix having a T_g of greater than 300°C.

25. The material of Claim 24 having a dielectric constant less than 2.5.

26. The material of Claim 24 having a dielectric constant less than 2.2.

27. The material of Claim 24 wherein the average diameter of the pores is
35 less than 400 nm.

28. The material of Claim 24 wherein the average diameter of the pores is less than 20 nm.

29. The material of Claim 24 pores occupy at least 10 volume percent of the material.

5 30. The material of Claim 24 which is a film having a thickness less than 10 microns.

31. The material of Claim 24 which is a polyarylene.

32. An article comprising a substrate and the material of Claim 31.

33. The article of Claim 32 wherein the material is a polyarylene.

10 34. An integrated circuit article comprising an active substrate containing transistors and an electrical interconnect structure containing patterned metal lines separated, at least partially, by layers or regions of a porous dielectric material, wherein the dielectric material is a cross-linked hydrocarbon-containing matrix having a T_g of greater than 300°C.

15 35. The article of Claim 34 wherein the cross-linked resin is a cured product of a polycyclopentadienone function compound and a polyacetylene functional compound.

36. The article of Claim 32 which is a liquid crystal display device.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/27674

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08L65/00 C08J9/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C08G C08J H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 776 990 A (HOFER DONALD CLIFFORD ET AL) 7 July 1998 (1998-07-07) cited in the application *** examples *** column 2, line 54 - column 3, line 17	1,2,7-9, 14,18, 19,22-30
A	US 5 785 787 A (WOJNAROWSKI ROBERT JOHN ET AL) 28 July 1998 (1998-07-28) column 2, line 52 - line 67	1-3
A	WO 98 11149 A (DOW CHEMICAL CO) 19 March 1998 (1998-03-19) cited in the application page 13, line 19 - line 25	1-36

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. nat Application No

PCT/US 99/27674

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